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STATEMENT UNDER 37 C.F.R. § 1.55

Sir,

I, Daisuke MORINO, hereby declare that I am conversant with both English and Japanese languages, and certify to best of my knowledge and belief that the attached is a true and correct English translations of Japanese Patent Application Nos. 2003-009905, 2003-028678, 2003-028679, 2003-029571 and 2003-038280 filed in the Japanese Patent and Trademark Office on January 17, 2003, February 5, 2003, February 5, 2003, February 6, 2003 and February 17, 2003, respectively, in the Japanese language.

Daisuke MORINO

Date: December 23, 2005

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This is to certify that the annexed is a true copy of
the following application as filed with this Office.

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[Title of the Invention] TONER AND IMAGE-FORMING APPARATUS
USING THE TONER

[Claims]

[Claim 1] A toner comprising negatively electrifiable toner mother particles having externally added thereto positively electrifiable silica fine particles, titanium oxide fine particles and particles comprising a long chain fatty acid or a salt of it.

[Claim 2] The toner as claimed in claim 1, wherein the toner mother particles have a quantity of electrification of from -5 to -60 $\mu\text{C/g}$.

[Claim 3] The toner as claimed in claim 1 or 2, wherein the positively electrifiable silica fine particles, titanium oxide fine particles, and particles comprising a long chain fatty acid or a salt of it are externally added to the toner mother particles at the same time.

[Claim 4] The toner as claimed in claim 1 or 2, wherein the positively electrifiable silica fine particles are externally added to the toner mother particles, and then the titanium oxide fine particles and particles comprising a long chain fatty acid or a salt of it are externally added at the same time.

[Claim 5] The toner as claimed in any of claims 1 to 4, wherein the positively electrifiable silica fine particles and the titanium oxide fine particles are added

in a mass ratio of from 1/3 to 3/1.

[Claim 6] An image-forming apparatus which is stocked with the toner as claimed in any of claims 1 to 5.

[Claim 7] The image-forming apparatus as claimed in claim 6, which is at least equipped with a latent image carrier on which an electrostatic latent image is formed; a toner carrier for carrying a toner to the latent image carrier for developing the electrostatic latent image on the latent image carrier; and a developing chamber having a toner regulating member to regulate the amount of the toner carried to the latent image carrier by the toner carrier.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a toner which is used for developing an electrostatic latent image in electrophotography, electrostatic recording and electrostatic printing and for forming an image by thermal fixation, and also relates to an image-forming apparatus using the toner.

[0002]

[Background Art]

The toner for forming electrostatic images generally comprises, as the toner mother particles, fine particles of a binding resin containing a coloring component, e.g., a dye or a pigment, and, if necessary, an electrification

controlling agent, and the toner is manufactured by a method of adding external additives to the outside (surface) of the toner mother particles for the purpose of providing flowability or controlling an electrification property. As the external additives, positively electrifiable silica fine particles, negatively electrifiable silica fine particles, inorganic fine particles other than silica (e.g., titanium oxide), fatty acid metal salt and the like are used.

[0003]

In general, the toner for forming electrostatic images is negatively electrified. Such a toner is manufactured by the method of preparing negatively electrifiable toner mother particles and adding external additives, e.g., positively electrifiable silica fine particles, etc., to the negatively electrifiable toner mother particles, to thereby control the quantity of negative electrification (refer to, e.g., patent literature 1 to 3). Alternatively, when from weakly negatively electrifiable toner mother particles to positively electrifiable toner mother particles are used, there is a method of adding external additives, such as negatively electrifiable silica fine particles, etc., to the above toner mother particles to control the quantity of negative electrification (refer to, e.g., patent literature 4 to 6).

[0004]

As the methods of manufacturing a toner by using negatively electrifiable toner mother particles, a method of externally adding positively electrifiable hydrophobic silica fine particles to toner mother particles comprising a negatively electrifiable binding resin,, a method of externally adding positively electrifiable hydrophobic silica fine particles and negatively electrifiable hydrophobic silica fine particles (refer to, e.g., patent literature 1 and 2), and a method of externally adding positively electrifiable hydrophobic silica fine particles and inorganic fine particles having a low electrical resistance value (refer to, e.g., patent literature 3) are exemplified.

[0005]

In general, electrification or flowability can be controlled by using external additives. However, in the toners obtained by the above method, external additives are liable to be desorbed from the surface of the toner, which causes the reduction of flowability or electrification property of the toners, as a result, transfer efficiency and image density are depressed.

[0006]

On the other hand, when weakly negatively electrifiable to positively electrifiable toner mother particles are used in manufacturing a toner, external addition methods are also examined. For example, a method

of externally adding positively electrifiable hydrophobic silica fine particles and negatively electrifiable hydrophobic silica fine particles at the same time (refer to, e.g., patent literature 4), and a method of externally adding a first component, a second component, a third component and a fourth component to toner mother particles at the same time, or externally adding the first component lastly, taking hydrophobic silica fine particles or hydrophobic titania as the first component, hydrophobic silica fine particles or hydrophobic titania having larger particle sizes than the particle sizes of component 1 as the second component, inorganic fine particles as the third component, and a fatty acid metal salt as the fourth component (refer to, e.g., patent literature 5) are known. Further, there is disclosed in a patent literature a method to obtain a toner in which the liberation of external additives is restrained by externally adding in the order of titanium oxide fine particles and silica fine particles to toner mother particles (refer to, e.g., patent literature 6).

[0007]

However, in the methods, external additives are liable to be desorbed from the surface of the toner, which causes the reduction of flowability or electrification property of the toners, as a result, transfer efficiency and image density are depressed.

[0008]

[Patent literature 1]

JP-A-2000-267337 (the term "JP-A" as used herein means an "unexamined published Japanese patent application").

[Patent literature 2]

JP-A-2002-14487

[Patent literature 3]

JP-A-2002-214834

[Patent literature 4]

JP-A-11-231571

[Patent literature 5]

JP-A-2001-100452

[Patent literature 6]

JP-A-2002-72544

[Patent literature 13]

JP-A-2002-202622

[0009]

[Problems to be Resolved by the Invention]

An object of the invention is to provide a toner which is low in desorption of positively electrifiable silica fine particles, negatively electrifiable silica fine particles, which can maintain the electrification property for a long period of time, shows high flowability and

transfer efficiency from the start material of a negatively chargeable toner mother particle.

[0010]

[Means of Solving the Problems]

The present invention provides a toner which is obtained by externally adding positively electrifiable silica fine particles, titanium oxide fine particles and particles comprising a long chain fatty acid or a salt of it to negatively electrifiable toner mother particles.

[0011]

In a preferred embodiment of the present invention, the toner mother particles have a quantity of electrification of from -5 to -60 $\mu\text{C/g}$.

[0012]

In a more preferred embodiment of the invention, the positively electrifiable silica fine particles, titanium oxide fine particles, and particles comprising a long chain fatty acid or a salt of it are externally added to the toner mother particles at the same time.

[0013]

In another preferred embodiment, the positively electrifiable silica fine particles are externally added to the toner mother particles, and then the titanium oxide fine particles and particles comprising a long chain fatty acid or a salt of it are externally added at the same time.

[0014]

In a further preferred embodiment, the positively electrifiable silica fine particles and the titanium oxide fine particles are added in a mass ratio of from 1/3 to 3/1.

[0015]

The present invention also relates to an image-forming apparatus which uses any of the above toners.

[0016]

In a still further preferred embodiment, the image-forming apparatus is at least equipped with a latent image carrier on which an electrostatic latent image is formed; a toner carrier for carrying a toner to the latent image carrier for developing the electrostatic latent image on the latent image carrier; and a developing chamber having a toner regulating member to regulate the amount of the toner carried to the latent image carrier by the toner carrier.

[0017]

[Detailed Description of the Preferred Embodiment]

The toner of the present invention can be obtained by externally adding positively electrifiable silica, titanium oxide and particles comprising a long chain fatty acid or a salt of it to negatively electrifiable toner mother particles, preferably toner mother particles having a quantity of electrification of from -5 to -60 $\mu\text{C/g}$. If necessary, inorganic fine particles other than titanium oxide are externally added.

[0018]

The materials which are used in the invention, e.g., (i) toner mother particles and the materials constituting the toner mother particles (so-called internal additives, e.g., binding resins, colorants, mold releasing agents, dispersants, electrification controlling agents, and magnetic agents), (ii) negatively electrifiable silica fine particles, (iii) positively electrifiable silica fine particles, (iv) titanium oxide fine particles, (v) long chain fatty acids or salts thereof, and (vi) inorganic fine particles which are added according to necessity, are described in the first place, and then the toner of the present invention is described.

[0019]

(i) Negatively electrifiable toner mother particles:

The toner mother particles which are used in the present invention are negatively electrified. A preferred quantity of electrification is from -5 to -60 $\mu\text{C/g}$. When the quantity of electrification is smaller than this range, the leakage of the toner from the developing chamber becomes conspicuous, while when the quantity of electrification is greater than -60 $\mu\text{C/g}$, there arises a new problem that excess development bias must be given to obtain sufficient image density.

[0020]

Negatively chargeable toner mother particles contain a binding resin and a colorant and, if necessary, internal

additives, e.g., a positively or negatively electrification controlling agent, a mold releasing agent, a dispersant, and a magnetic agent.

[0021]

There are some methods to electrify toner mother particles so as to have an appropriate range of the quantity of negative electrification. For example, a method of making a binding resin itself negatively electrifiable resin, a method of further blending a negative electrification controlling agent when the electrification property of a negatively electrifiable resin is not sufficient, or a method of blending a negative electrification controlling agent with a positively electrifiable binding resin.

[0022]

(Binding resins)

Considering the methods of electrifying toner mother particles negatively, any of positively electrifiable resins and negatively electrifiable resins, which are generally used as a material of toner, can be used as binding resins. As such resins, for example, polystyrene-based resins, acrylate-based resins or methacrylate-based resins (hereinafter referred to as (meth)acrylate-based resins), styrene-acrylic-based resins, polyester resins, polyethylene resins, epoxy resins, silicone resins, polypropylene resins, fluorine resins, polyamide resins,

polyvinyl alcohol resins, polyurethane resins, polyvinyl butyral resins, and copolymers containing the constituents of these resins are used.

[0023]

Among them, the case wherein the binding resin itself is negatively chargeable is explained. As negatively electrifiable resins, resins having a substituent, e.g., a carboxyl group, a phenyl group, a thiophenyl group or a sulfonic acid group, on the side chain are preferably used. It is preferred that these substituents take the form of a metal salt. As the metal salt, a metal salt with zinc, magnesium, aluminum, sodium, potassium, chromium, iron, manganese or cobalt is preferred. Alternatively, these substituents may be in the form of a salt with an organic base, e.g., an ammonium ion, a pyridinium ion or an imidazolium ion.

[0024]

As the negatively electrifiable resins, polyester resins are most preferably used. Such polyester resins have a carboxyl group on the side chain which can be obtained by polycondensation of polyhydric alcohols with polyvalent carboxylic acids or derivatives thereof.

[0025]

As the polyhydric alcohols which constitute polyester resins, dihydric alcohols, trihydric alcohols or tetrahydric or higher alcohols are used.

[0026]

The examples of dihydric alcohols include ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, dipropylene glycol, ethylene oxide adducts of bisphenol A and propylene oxide adducts of bisphenol A.

[0027]

The examples of trihydric alcohols include glycerol, trimethylolpropane, trimethylolethane, 1,2,4-butanetriol, 1,2,5-pentanetriol, 2-methylpropanetriol, 2-methyl-1,2,4-butanetriol, and 1,3,5-trihydroxymethylbenzene.

[0028]

The examples of tetrahydric or higher alcohols include sorbitol, 1,2,3,6-hexanetetraol, 1,4-sorbitan, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0029]

These polyhydric alcohols are used alone or as mixtures. Of these polyhydric alcohols, neopentyl glycol, trimethylolpropane, ethylene oxide adducts of bisphenol A and propylene oxide adducts of bisphenol A are preferably used.

[0030]

As the polyvalent carboxylic acids which constitute the polyester resins, divalent carboxylic acids, trivalent or higher carboxylic acids and derivatives of these

carboxylic acids are exemplified.

[0031]

The examples of divalent carboxylic acids include malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, phthalic acid, terephthalic acid and isophthalic acid. As the derivatives of divalent carboxylic acids, lower alkyl esters and acid anhydrides of these acids are used. As the lower alkyl esters, alkyl esters having from 1 to 12 carbon atoms, e.g., methyl esters and ethyl esters are preferably used.

[0032]

Of these divalent carboxylic acids, divalent carboxylic acids having an aromatic ring, e.g., phthalic acid, terephthalic acid, isophthalic acid, lower alkyl esters and acid anhydrides of these acids are preferably used.

[0033]

The examples of trivalent or higher carboxylic acids include 1,2,4-benzenetricarboxylic acid, 1,2,5-benzenetricarboxylic acid, 1,2,4-cyclohexanetricarboxylic acid, 2,5,7-naphthalenetricarboxylic acid, 1,2,4-naphthalenetricarboxylic acid, 1,2,4-butanetricarboxylic acid, 1,2,5-hexatricarboxylic acid, 1,3-dicarboxyl-2-methyl-2-methylenecarboxypropane, tetra(methylenecarboxyl)methane, 1,2,7,8-octanetetracarboxylic acid, and pyromellitic acid.

As the derivatives of these trivalent or higher carboxylic acids, lower alkyl esters and acid anhydrides of these carboxylic acids are exemplified.

[0034]

The manufacturing methods of polyester resins are not particularly restricted, and they are manufactured by polycondensation of polyvalent carboxylic acids and polyhydric alcohols by the methods usually used in this industry. In polycondensation, the reacting weight of polyvalent carboxylic acids and polyhydric alcohols is preferably from 0.8 to 1.4 in the molar ratio of hydroxyl group to carboxyl group (OH/COOH). Further, it is preferred to adjust the acid value of the obtained polyester resin to 1 to 100, more preferably from 1 to 30. When the acid value is smaller than 1, the dispersibility of internal additives, e.g., an electrification controlling agent, a mold releasing agent and a colorant, to the binding resin is reduced. When the acid value is higher than 100, the moisture resistance of the toner lowers. In addition, an acid value is measured by ordinary methods with KOH.

[0035]

When the above polyester resin is used as the binding resin and, in particular, when offset resistance and transparency (smoothness of the fixed image) of a high level are desired, it is preferred to use a urethane-

modified polyester resin as the polyester resin.

[0036]

A urethane-modified polyester resin can be obtained by the reaction of a polyester resin with an isocyanate. The reaction is performed by the methods usually used in this industry. In the reaction, it is preferred to blend them so that the isocyanate becomes from 0.3 to 0.99 molar equivalent per molar equivalent of the hydroxyl group of a polyester resin, more preferably from 0.5 to 0.95 molar equivalent. When the molar ratio of the isocyanate is less than 0.3, the offset resistance may decrease. While when the molar ratio is more than 0.99, the viscosity conspicuously increases, so that stirring is sometimes difficult.

[0037]

Isocyanates are not particularly limited, but hexamethylene diisocyanate, isophorone diisocyanate, tolylene diisocyanate, diphenylmethane diisocyanate, xylylene diisocyanate, and tetramethylxylylene diisocyanate are preferably used.

[0038]

The mass average molecular weight of the binding resins which are used in the present invention is not especially restricted, but it is generally preferably from 2,000 to 30,000, more preferably from 4,000 to 25,000, and still more preferably from 6,000 to 20,000. When the

molecular weight is less than 2,000, the viscosity lowers at blending, and a colorant cannot be dispersed sufficiently in some cases. Therefore, the chroma or transparency of the obtained toner is liable to lower. When the molecular weight is greater than 30,000, the viscosity becomes too high, so that a colorant cannot be dispersed sufficiently and the chroma or transparency of the toner is sometimes reduced. A plurality of binding resins having the above molecular weight may be mixed.

[0039]

The molecular weight of binding resins is measured by gel permeation chromatography (GPC).

[0040]

When a toner is fixed by thermal fixation in image formation, the flow softening point (T_m) of a binding resin is preferably low. T_m is preferably from 85 to 140°C, more preferably from 90 to 120°C, and still more preferably from 100 to 110°C. The glass transition temperature (T_g) of a binding resin is preferably from 40 to 90°C, more preferably from 50 to 80°C. A flow softening point (T_m) is measured by using a sample obtained by pressure-molding 1.0 g of a binding resin to make a pellet, with "Flow Tester CFT-500D" (a product of Shimadzu Corporation) on conditions of: heat-up velocity of 5°C/min; cylinder pressure of 2.0 MPa; the hole diameter of a die of 1.0 mm; the hole length of a die of 1.0 mm; and by T_m computing

method of a 1/2 method. Further, the glass transition temperature (T_g) of a binding resin is measured by packing 10 mg of a binding resin in an aluminum cell and with "DSC120" (a product of Seiko Instruments Inc.) on conditions of: measuring temperature of from 0 to 200°C; and heat-up velocity of 10°C/min; and the value is read from the DSC curve of the second heat-up time.

[0041]

When a toner is fixed by pressure fixation, wax-like resins are preferably used as the binding resin. Of the above binding resins, polyethylene resins, polyethylene-vinyl acetate copolymers and natural waxes are used as the wax-like resins.

[0042]

The binding resins are manufactured by polymerization, e.g., emulsion polymerization, dispersion polymerization and suspension polymerization, or pulverization including kneading, pulverization and classification processes. Considering the homogeneity and flowability of the finally obtained toner particles, the binding resins obtained by polymerization are preferably used.

[0043]

The binding resins may be used alone or two or more binding resins may be blended. The above-shown binding resins are representative examples and the present invention is not of course limited thereto.

[0044]

(Colorants)

As colorants, the following-shown organic pigments, inorganic pigments and dyes are used. Of organic and inorganic pigments, carbon black, copper oxide, tri-iron tetroxide, manganese dioxide, Aniline Black and active carbon are used as black pigments.

[0045]

As yellow pigments, chrome yellow, zinc yellow, cadmium yellow, yellow iron oxide, mineral fast yellow, nickel titan yellow, naples yellow, Naphthol Yellow S, Hansa Yellow, Benzidine Yellow G, Benzidine Yellow GR, Quinoline Yellow Lake, Permanent Yellow NCG, and Tartrazine Lake are used.

[0046]

As orange pigments, red chrome yellow, molybdenum orange, Permanent Orange GTR, Pyrazolone Orange, Vulcan Orange, Indanthrene Brilliant Orange RK, Benzidine Orange G, and Indanthrene Brilliant Orange GKM are used.

[0047]

As red pigments, iron oxide red, cadmium red, red lead, mercury sulfide, cadmium, Permanent Red 4R, Lithol Red, Pyrazolone Red, Watchung Red, calcium salt, Lake Red D, Brilliant Carmine 6B, eosine lake, Rhodamine Lake B, Alizarine Lake and Brilliant Carmine 3B are used.

[0048]

As violet pigments, manganese violet, Fast Violet B and Methyl Violet Lake are used. As blue pigments, Prussian blue, cobalt blue, Alkali Blue Lake, Victoria Blue Lake, Phthalocyanine Blue, nonmetal Phthalocyanine Blue, partially chlorinated product of Phthalocyanine Blue, Fast Sky Blue and Indanthrene Blue BC are used.

[0049]

As green pigments, chrome green, chromium oxide, Pigment Green B, Malachite Green Lake and Final Yellow Green G are used.

[0050]

As white pigments, zinc flower, titanium oxide, antimony white and zinc sulfide are used.

[0051]

As extender pigments, baryta powder, barium carbonate, clay, silica, white carbon, talc and alumina white are used.

[0052]

As dyes, basic dyes, acid dyes, dispersed dyes and direct dyes are used. The examples of such dyes include Nigrosine, Methylene Blue, Rose Bengale, Quinoline Yellow and Ultramarine Blue.

[0053]

When the toner of the present invention is a transparent color toner, the following-shown various pigments and dyes are used as the colorants.

[0054]

As yellow pigments, C.I. 10316 (Naphthol Yellow S), C.I. 11710 (Hansa Yellow 10G), C.I. 11660 (Hansa Yellow 5G), C.I. 11670 (Hansa Yellow 3G), C.I. 11680 (Hansa Yellow G), C.I. 11730 (Hansa Yellow GR), C.I. 11735 (Hansa Yellow A), C.I. 11740 (Hansa Yellow NR), C.I. 12710 (Hansa Yellow R), C.I. 12720 (Pigment Yellow L), C.I. 21090 (Benzidine Yellow), C.I. 21095 (Benzidine Yellow G), C.I. 21100 (Benzidine Yellow GR), C.I. 20040 (Permanent Yellow NCG), C.I. 21220 (Vulcan Fast Yellow 5) and C.I. 21135 (Vulcan Fast Yellow R) are used.

[0055]

As red pigments, C.I. 12055 (Stirling I), C.I. 12075 (Permanent Orange), C.I. 12175 (Lithol Fast Orange 3GL), C.I. 12305 (Permanent Orange GTR), C.I. 11725 (Hansa Yellow 3R), C.I. 21165 (Vulcan Fast Orange GG), C.I. 21110 (Benzidine Orange G), C.I. 12120 (Permanent Red 4R), C.I. 1270 (Para Red), C.I. 12085 (Fire Red), C.I. 12315 (Brilliant Fast Scarlet), C.I. 12310 (Permanent Red F2R), C.I. 12335 (Permanent Red F4R), C.I. 12440 (Permanent Red FRL), C.I. 12460 (Permanent Red FRLl), C.I. 12420 (Permanent Red F4RH), C.I. 12450 (Light Fast Red Toner B), C.I. 12490 (Permanent Carmine FB), and C.I. 15850 (Brilliant Carmine 6B) are used.

[0056]

As blue pigments, C.I. 74100 (nonmetal

Phthalocyanine Blue), C.I. 74160 (Phthalocyanine Blue), and C.I. 74180 (Fast Sky Blue) are used.

[0057]

These colorants may be used alone or a plurality of colorants may be used in combination. The colorants are used in an amount of from 1 to 20 mass% to 100 mass% of the binding resin, preferably from 2 to 10 mass%. When the amount of colorants is more than 20 mass%, the fixing property and transparency of the toner decrease, while when the amount is less than 1 mass%, there is a risk of incapability of obtaining desired image density.

[0058]

(Mold releasing agents)

As the mold releasing agent, paraffin-based waxes, polyolefin-based waxes, modified waxes having an aromatic group, hydrocarbon compounds having an alicyclic group, natural waxes, long chain fatty acids having 12 or more carbon atoms, the esters thereof, metal salts of long chain fatty acids (metal soaps), fatty acid amide and fatty acid bisamide are used. Of the above mold releasing agents, paraffin-based waxes, polyolefin-based waxes and metal soaps are preferably used.

[0059]

The examples of paraffin-based waxes include, e.g., paraffin wax (manufactured by Nippon Oil Co., Ltd. and Nippon Seiro Co., Ltd.), micro-wax (manufactured by Nippon

Oil Co., Ltd.), micro-crystalline wax (manufactured by Nippon Seiro Co., Ltd.), hard paraffin wax (manufactured by Nippon Seiro Co., Ltd.), PE-130 (manufactured by Hoechst A.G.), Mitsui High Wax 110P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 220P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 660P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 210P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 320P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 410P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 420P (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-1142 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-2130 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-4020 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-1142 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-5020 (manufactured by Mitsui Petrochemical Industries, Ltd.), beeswax, carnauba wax and montan wax.

[0060]

As polyolefin-based waxes, e.g., low molecular weight polypropylene, low molecular weight polyethylene, oxidation type polypropylene and oxidation type polyethylene are exemplified. The specific examples of

polyolefin-based waxes include non-oxidation type polyethylene waxes, e.g., Hoechst Wax PE520, Hoechst Wax PE130, Hoechst Wax PE190 (manufactured by Hoechst A.G.), Mitsui High Wax 200, Mitsui High Wax 210, Mitsui High Wax 210M, Mitsui High Wax 220, Mitsui High Wax 220M (manufactured by Mitsui Petrochemical Industries, Ltd.), SANWAX 131-P, SANWAX 151-P, and SANWAX 161-P (manufactured by Sanyo Chemical Industries Co., Ltd.), oxidation type polyethylene waxes, e.g., Hoechst Wax PED121, Hoechst Wax PED153, Hoechst Wax PED521, Hoechst Wax PED522, Hoechst Wax Ceridust 3620, Hoechst Wax Ceridust VP130, Hoechst Wax Ceridust VP5905, Hoechst Wax Ceridust VP9615A, Hoechst Wax Ceridust TM9610F, Hoechst Wax Ceridust 3715 (manufactured by Hoechst A.G.), Mitsui High Wax 420M (manufactured by Mitsui Petrochemical Industries, Ltd.), SANWAX E-300 and SANWAX E-250P (manufactured by Sanyo Chemical Industries Co., Ltd.), non-oxidation type polypropylene waxes, e.g., Hoechst Wachs PP230 (manufactured by Hoechst A.G.), and VISCOL 330-P, VISCOL 550-P, VISCOL 660-P (manufactured by Sanyo Chemical Industries Co., Ltd.), and oxidation type polypropylene waxes, e.g., VISCOL TS-200 (manufactured by Sanyo Chemical Industries Co., Ltd.).

[0061]

These mold releasing agents may be used alone or a plurality of compounds may be used in combination. Mold releasing agents having a low softening point (melting

point), e.g., from 40 to 130°C, preferably from 50 to 120°C, are preferably used. A softening point is represented by an endothermic main peak value on the DSC endothermic curve measured with "DSC120" (a product of Seiko Instruments Inc.).

[0062]

As the examples of fatty acid metal salts (metal soaps), e.g., zinc stearate, calcium stearate, magnesium stearate, zinc oleate, zinc palmitate and magnesium palmitate are preferably used.

[0063]

(Electrification controlling agents)

An electrification controlling agent is used for controlling the electrification property of toner mother particles, according to necessity. When the degree of a negative electrification property of a binding resin itself is low or when a binding resin itself is positively electrified, a negative electrification controlling agent is used, so that the toner mother particles at large have a desired level of a negative electrification property. As negative electrification controlling agents, metal salts or metal complexes of salicylic acid derivatives, metal salts of benzilic acid derivatives, and phenyl borate quaternary ammonium salts are exemplified. As the metal salts of salicylic acid derivatives or benzilic acid derivatives, zinc salts, nickel salts, copper salts and chromium salts

of these derivatives are preferably used.

[0064]

The examples of commercially available negative electrification controlling agents include, e.g., Oil Black (Color Index 26150), Oil Black BY (manufactured by Orient Chemical Industry Co., Ltd.), Bontron S-22 (manufactured by Orient Chemical Industry Co., Ltd.), salicylic acid metal complex E-81 (manufactured by Orient Chemical Industry Co., Ltd.), thioindigo series pigments, sulfonylamine derivatives of copper phthalocyanine, Spiron Black TRH (manufactured by HODOGAYA CHEMICAL Co., Ltd.), Bontoron S-34 (manufactured by Orient Chemical Industry Co., Ltd.), Nigrosine SO (manufactured by Orient Chemical Industry Co., Ltd.), Celesschwarz (R)G (manufactured by Farbenfabriken Bayer A.G.), Chromogeneschwarz ETOO (C.I. No. 14645), and Azo Oil Black (R) (manufactured by National Aniline Co.). Of these products, salicylic acid metal complex E-81 is preferably used. These negative electrification controlling agents can be used alone or a plurality of compounds may be used in combination.

[0065]

A negative electrification controlling agent is preferably blended with a binding resin so that the quantity of electrification of toner mother particles becomes from -5 to -60 $\mu\text{C/g}$. Accordingly, the addition amount of a negative electrification controlling agent is

decided by the binding resin used, but generally the amount is from 0.1 to 5 mass parts to 100 mass parts of the binding resin.

[0066]

A positive electrification controlling agent is internally added to a negative electrifiable resin for the purpose of adjusting the quantity of negative electrification of toner mother particles, if necessary. As the positive electrification controlling agents, commercially available products are used. For example, Nigrosine Base EX (manufactured by Orient Chemical Industry Co., Ltd.), a quaternary ammonium salt P-51 (manufactured by Orient Chemical Industry Co., Ltd.), Nigrosine Bontoron N-01 (manufactured by Orient Chemical Industry Co., Ltd.), Sudan Chief Schwarz BB (Solvent Black 3: Color Index 26150), Fetschwarz HBN (C.I. No. 26150), Brilliant Spirits Schwarz TN (manufactured by Farbenfabriken Bayer A.G.), and Zaponschwarz X (manufactured by Farberke Hoechst A.G.) are exemplified. Of these products, a quaternary ammonium salt P-51 is preferably used. In addition to the above products, alkoxylated amine, alkylamide and chelate pigments of molybdic acids are also used as a positive electrification controlling agent. These positive electrification controlling agents may be used alone or a plurality of compounds may be used in combination.

[0067]

(Dispersants)

Metal soaps and polyethylene glycol and the like are used as the dispersant.

[0068]

(Magnetic agents)

As magnetic agents, metallic powders of, e.g., Fe, Co, Ni, Cr, Mn and Zn, metallic oxides, e.g., Fe_3O_4 , Fe_2O_3 , Cr_2O_3 , ferrite, and alloys showing ferromagnetism by thermal treatment, e.g., alloys containing manganese and acid, are exemplified. These magnetic agents may be subjected to treatment in advance with a coupling agent.

[0069]

(Manufacture of toner mother particles)

Toner mother particles are manufactured by adding a colorant and, if necessary, internal additives, e.g., a mold releasing agent, a dispersant, an electrification controlling agent, and a magnetic agent, to a binding resin. In the present invention, quantity of electrification of toner mother particles is adjusted to preferably -5 to -60 $\mu\text{C/g}$, if necessary, by using a negative electrification controlling agent.

[0070]

For example, a method of manufacturing mother particles by a pulverizing method including kneading, pulverization and classification processes is described below. Firstly, a binding agent, a colorant and additives,

e.g., a mold releasing agent, in prescribed amounts are introduced into a mixer, e.g., Henschel Mixer 20B (a product of MITSUI MINING COMPANY, LIMITED) and blended homogeneously. The blending ratios of additives, e.g., a binding resin, a colorant, an electrification controlling agent, and a mold releasing agent, are decided arbitrarily taking the color and electrification property of the toner into consideration.

[0071]

The above mixture is then introduced into a twin-screw kneading extruder (PCM-30, manufactured by IKGAI KASEI CO., LTD) and homogeneously melt kneaded. As the melt-kneading means besides the above, continuous kneaders, e.g., "TEM-37" (manufactured by TOSHIBA MACHINE CO., LTD.) and "KRC Kneader" (manufactured by KURIMOTO, LTD.), and batch type kneaders, e.g., a hot-pressing kneader, are exemplified. Toner mother particles having a desired average particle size can be obtained by pulverizing the obtained melt-kneaded product by means of a grinding means. Pulverization is performed by, e.g., impinging pulverization by jet air using a jet pulverizer 200AFG (a product of HOSOKAWA MICRON CORPORATION) or IDS-2 (a product of Nippon Pneumatic Mfg Co., Ltd.), in addition, by a mechanical pulverizer Turbo Mill (a product of Kawasaki Heavy Industries, Ltd.) or Super Rotor (a product of Nisshin Engineering), etc.

[0072]

In the next place, the particle size of the obtained toner mother particles is adjusted by wind power or rotation of rotors. For instance, a sharp particle size distribution can be obtained by using, e.g., a wind power classifier 100ATP (a product of HOSOKAWA MICRON CORPORATION), DSX-2 (a product of Nippon Pneumatic Mfg Co., Ltd.), or Elbow-Jet (a product of NITTETSU MINING CO., LTD.).

[0073]

Toner mother particles may also be manufactured by a method of dissolving internal additives constituting the toner mother particles, e.g., a resin and a colorant, in an organic solvent, dispersing and granulating the aqueous solvent with a classifying agent and an emulsifying agent, and then separating and drying the emulsion.

[0074]

The measurement of the quantity of electrification is performed as follows. For instance, the quantity of electrification of toner mother particles is measured as follows. Under the environment at 25°C, 45% RH, 0.03 g of toner mother particles and 0.97 g of a ferrite carrier are mixed in a polyethylene vessel having a capacity of 20 ml and stirred for 15 minutes at 100 rpm, to thereby electrify the toner mother particles. Subsequently, 0.3 g of the mixture is taken out, and nitrogen gas of the pressure of

0.3 kg/cm² is blown to the mixture of the toner mother particles and the carrier, to thereby separate the toner mother particles and the ferrite carrier. After that, the quantity of electrification of every toner (Q/m) is measured and the quantity of electrification of toner mother particles is computed from that. The measurement of the quantity of electrification is performed with, e.g., E-SPART Analyzer (a product of HOSOKAWA MICRON CORPORATION).

[0075]

(ii) Positively electrifiable silica fine particles:

Positively electrifiable silica fine particles which are used in the present invention are not especially limited. The volume average particle size of positively electrifiable silica fine particles is preferably from 10 to 50 nm, more preferably from 15 to 40 nm, taking the flowability and the like into consideration.

[0076]

It is preferred that positively electrifiable silica fine particles be subjected to hydrophobitization treatment. By making the surfaces of positively electrifiable silica fine particles hydrophobic, the flowability and chargeability of the toner can be improved. The hydrophobitization of positively electrifiable silica fine particles is carried out according to the same method as the hydrophobitization of negatively electrifiable silica fine particles.

[0077]

As positively electrifiable hydrophobic silica fine particles, commercially available NA50H (manufactured by Nippon Aerosil Co., Ltd.) and TG820F (manufactured by Cabot) are used.

[0078]

(iv) Titanium oxide (titania) fine particles:

Titanium oxide fine particles for use in the present invention are not particularly limited. Titanium oxide fine particles having a relatively small electrical resistivity are preferably used. Titanium oxide may take a crystal form of rutile type, anatase type, rutile-anatase type. Titanium oxide of any crystal form may be used, but titanium oxide of a rutile-anatase type is preferably used for the reason that the adjustment of electric charge is easy and a rutile-anatase type titanium oxide is difficult to be buried in toner mother particles even when the number of sheets of printing increases.

[0079]

The size of titanium oxide fine particles is not particularly restricted but it is preferred that the particle size or long axis length be 10 to 30 nm. In the case of a rutile-anatase type titanium oxide, titanium oxide fine particles having a long axis length of about 20 nm are preferred.

[0080]

By making the surfaces of titanium oxide fine particles hydrophobic, a stable electrification property can be maintained, and the flowability of the toner can be improved. The hydrophobitization of titanium oxide fine particles is carried out according to the same method as the hydrophobitization of negatively electrifiable silica fine particles.

[0081]

As hydrophobic titanium oxide fine particles, STT-30S (manufactured by TITAN KOGYO KABUSHIKI KAISHA) and the like are used.

[0082]

(iv) Long chain fatty acids or salts thereof

The long chain fatty acids or salts thereof for use in the present invention are not particularly restricted. As the long chain fatty acids, long chain fatty acids preferably having from 10 to 30 carbon atoms, more preferably from 12 to 28 are used. As the long chain fatty acids, long chain saturated fatty acids and long chain unsaturated fatty acids are exemplified. Long chain saturated fatty acids are preferably used. The long chain fatty acids may be branched, but long chain saturated fatty acids, e.g., stearic acid, is preferably used.

[0083]

It is preferred to use the long chain fatty acids in the form of salts, and more preferably in the form of metal

salts (so-called metal soaps). The metal salts of the long chain fatty acids are not particularly restricted and, e.g., calcium salts, zinc salts, magnesium salts, aluminum salts and lithium salts are exemplified. As the metal soaps, e.g., fine particles of magnesium stearate, calcium stearate and zinc stearate are preferably used. Particles comprising long chain saturated fatty acids or salts thereof may be used alone or as mixtures of two or more kinds.

[0084]

(v) Inorganic fine particles

Inorganic fine particles other than titanium oxide fine particles are also externally added for the purpose of controlling the electrification property and improving flowability. For instance, as inorganic fine particles, fine particles of metallic oxide, e.g., aluminum oxide, strontium oxide, tin oxide, zirconia oxide, magnesium oxide, and indium oxide; fine particles of nitrides, e.g., silicon nitride; fine particles of carbides, e.g., silicon carbide; fine particles of metal salts, e.g., calcium sulfate, barium sulfate and calcium carbonate; and inorganic fine particles of these are exemplified. Fine particles of metallic oxides having a relatively small electrical resistivity, e.g., $10^9 \Omega \cdot \text{cm}$ or less are preferably used.

[0085]

The sizes of inorganic fine particles added are not particularly restricted, but the sizes of from 10 to 30 nm are preferred. It is preferred that the surfaces of these inorganic fine particles be subjected to hydrophobitization treatment for the purpose of improving the stabilization of electrification characteristics. The hydrophobitization treatment of inorganic fine particles is performed by the same method as used in the hydrophobitization treatment of negatively electrifiable silica fine particles or positively electrifiable silica fine particles.

[0086]

(II) Toner of the present invention and manufacturing method:

The toner of the present invention can be obtained by externally adding positively electrifiable silica, titanium oxide and particles comprising a long chain fatty acid or a salt of it to negatively electrifiable toner mother particles. Further, by specifying the addition order of these additives, two kinds of toners (toner A and toner B) are manufactured. The quantity of electrification is generally adjusted so as to be from -7 to -30 $\mu\text{C/g}$.

[0087]

[Toner A]

Toner A can be obtained by adding positively electrifiable silica, titanium oxide and fatty acid or a metal salt thereof to negatively electrifiable toner mother

particles, preferably toner mother particles having a quantity of electrification of from -5 to -60 $\mu\text{C/g}$. The addition amounts of positively electrifiable silica, titanium oxide fine particles, and fatty acid or a metal salt thereof which are used in the manufacture of toner A are variable according to the particle size distribution or flowability of toner mother particles, the particle size distribution of external additives, and a desired quantity of electrification.

[0088]

Positively electrifiable silica fine particles are added in an amount of from 0.1 to 2.0 mass parts to 100 mass parts of the toner mother particles, and preferably from 0.3 to 1.5 mass parts.

[0089]

Titanium oxide fine particles are added in an amount of from 0.2 to 2.0 mass parts to 100 mass parts of the toner mother particles, and preferably from 0.3 to 1.5 mass parts.

[0090]

The positively electrifiable silica fine particles and the titanium oxide fine particles are preferably added in a mass ratio of from 1/3 to 3/1 for capable of adjusting electric charge without causing extreme reduction of the electrical resistance of the toner.

[0091]

The particles comprising a long chain fatty acid or a salt of it are added in an amount of from 0.1 to 1.0 mass part to 100 mass parts of the toner mother particles, and preferably from 0.1 to 0.5 mass parts.

[0092]

Further, if necessary, (v) inorganic fine particles may be added for the purpose of adjusting electric charge and improving flowability. The inorganic fine particles are preferably added simultaneously with positively electrifiable silica fine particles in view of the stabilization of electrification property.

[0093]

External addition of positively electrifiable silica fine particles, titanium oxide fine particles and a fatty acid or a salt thereof to toner mother particles is carried out by machines or methods usually used in this industry, e.g., high speed fluid mixers, such as a Henschel mixer or Perpenmyer, and mixers using a mechanochemical method. Toner A can be obtained, for example, by putting toner mother particles and negatively electrifiable silica fine particles into a Henschel mixer and stirring at a prescribed stirring velocity for prescribed time, introducing titanium oxide fine particles and further stirring at a prescribed stirring velocity for prescribed time, and finally introducing positively electrifiable silica fine particles and stirring at a prescribed stirring

velocity for prescribed time. The velocity and time of stirring in each process can be set independently, but the conditions may be the same.

[0094]

Since external additives having an electrification property are not included in the manufacturing method of toner A of the present invention other than positively electrifiable silica fine particles (e.g., negatively electrifiable silica fine particles), the static attraction between appropriately negatively electrified toner mother particles and positively electrifiable silica fine particles is not hindered, and the difference between the work function of positively electrifiable silica fine particles and the work function of toner mother particles is large, so that positively electrifiable silica fine particles can be strongly adhered to toner mother particles. Therefore, the desorption of positively electrifiable silica fine particles is prevented and the fluctuation of electrification property lessens, as a result, an electrification property can be stabilized for a long period of time.

[0095]

Titanium oxide fine particles have low electrical resistance, accordingly there is high possibility that the electric charge is excessively lost when titanium oxide fine particles are present on the surface of the toner. On

the other hand, positively electrifiable silica fine particles are positively electrified and have a high electrical resistance value. Therefore, by externally adding titanium oxide fine particles and positively electrifiable silica fine particles at the same time, the positively electrifiable silica fine particles function as the electric charge adjuster, and the reduction of the electrical resistivity of the toner is controlled and the electric charge is unified.

[0096]

It is thought that particles comprising a long chain fatty acid or a salt thereof functions as the binding agent of positively electrifiable silica fine particles and titanium oxide fine particles. Accordingly, the addition of particles comprising a long chain fatty acid or a salt thereof is effective to prevent desorption of the positively electrifiable silica fine particles and titanium oxide fine particles, and presumably takes effect in stabilization of electrification property for a long period of time.

[0097]

By adding these external additives at the same time, the above various effects are exhibited. Further, since positively electrifiable silica fine particles come to be liberated and present in the toner in an appropriate rate, the flowability of the toner becomes good and, at the same

time, the free positively electrifiable silica fine particles function as the carrier, so that the electrification property becomes more uniform. It is also thought that particles comprising a long chain fatty acid or a salt thereof have the effect to prevent coagulation of toner, and the function as the auxiliary flowing agent and lubricant.

[0098]

Toner A according to the present invention is thus obtained by the method of externally adding a fatty acid or a salt thereof in addition to positively electrifiable silica fine particles and titanium oxide fine particles at the same time, and has a uniform electrification property as compared with the case where positively electrifiable silica fine particles and/or titanium oxide fine particles are added to negatively electrifiable mother particles as disclosed in patent literature 1 to 3. Toner A has an excellent effect that uniform electrification property is stably maintained for a long period of time and excellent flowability is maintained for a long period of time as a result of preventing liberation of positively electrifiable silica fine particles or titanium oxide fine particles.

[0099]

[Toner B]

Toner B is obtained by externally adding positively electrifiable silica fine particles to toner mother

particles in the first place, and then titanium oxide fine particles and particles comprising a long chain fatty acid or a salt of it at the same time.

[0100]

Since external additives having an electrification property are not included in the manufacturing method of toner B of the present invention other than positively electrifiable silica fine particles (e.g., negatively electrifiable silica fine particles), the static attraction between negatively electrified toner mother particles and positively electrifiable silica fine particles is not hindered, and the difference between the work function of positively electrifiable silica fine particles and the work function of toner mother particles is large, so that positively electrifiable silica fine particles are strongly adhered to toner mother particles. Therefore, the desorption of positively electrifiable silica fine particles is prevented and the fluctuation of electrification property lessens, as a result, an electrification property can be stabilized for a long period of time.

[0101]

After the addition of positively electrifiable silica fine particles, titanium oxide fine particles and particles comprising a long chain fatty acid or a salt thereof are added, and by adding positively electrifiable

silica fine particles having a high electrical resistance value in advance, the surface electric charge of the toner does not lower greatly when titanium oxide fine particles having low electrical resistance are added (that is, the positively electrifiable silica fine particles function as the electric charge adjuster), the reduction of the electrical resistivity of the toner is controlled and the electric charge is unified. In addition to these effects, the long chain fatty acid or a salt thereof functions as the binding agent and effectively prevents the liberation of the positively electrifiable silica fine particles and the titanium oxide fine particles, and stabilizes electrification stability for a long period of time. Further, the long chain fatty acid or a salt thereof has the effect of preventing coagulation of toner, and functions as auxiliary flowing agent and lubricant.

[0102]

As described above, toner B of the present invention is obtained by the method of externally adding positively electrifiable silica fine particles first, and then titanium oxide fine particles and fatty acid or a salt thereof, and has a uniform electrification property as compared with the case where positively electrifiable silica fine particles and/or titanium oxide fine particles are added to negatively electrifiable mother particles as disclosed in patent literature 1 to 3. Toner B has an

excellent effect that uniform electrification property is stably maintained for a long period of time and excellent flowability is maintained for a long period of time as a result of preventing liberation of positively electrifiable silica fine particles or titanium oxide fine particles.

[0103]

The toners A and B of the invention can be used in any type of image-forming apparatus, e.g., image-forming apparatus using one-component series toners, or image-forming apparatus using two-component series toners, may be used. Image-forming apparatus of a contact development system or image-forming apparatus of a non-contact development system may also be used. Image-forming apparatus of a contact development system using one-component series toners capable of using the toner of the invention are described in detail, e.g., in patent literature 7. The image-forming apparatus of the present invention is equipped with at least a latent image carrier on which an electrostatic latent image is formed represented by a photosensitive material; a toner carrier for carrying a toner to the latent image carrier for developing the electrostatic latent image on the latent image carrier represented by a developing roller; and a developing chamber having a toner regulating member to regulate the amount of the toner carried to the latent image carrier by the toner carrier. The toner of the

present invention is held in a toner holder, carried from the toner holder to the developing roller (the toner carrier) and supplied to the photosensitive material (the latent image carrier) via the developing roller (the toner carrier), transferred, thereby an image is formed. The toner regulating member adjusts the amount of the toner so that an excess amount of the toner is not supplied to the photosensitive material (the latent image carrier) from the developing roller (the toner carrier).

[0104]

[Example]

The present invention is illustrated with reference to examples below.

[0105]

(Preparation of toner mother particles)

One hundred (100) mass parts of a binding resin comprising polyester and 3.5 mass parts of a red pigment (C.I. 12055) were put into Henschel Mixer 20B (a product of MITSUI MINING COMPANY, LIMITED), and homogeneously blended. The mixture was melt-kneaded with a two-shaft kneading extruder PCM-30 (manufactured by IKEGAI KASEI CO., LTD), and after cooling, pulverized by jet air with a jet pulverizer 200AFG (a product of HOSOKAWA MICRON CORPORATION). The pulverized product was classified with a wind power classifier 100ATP (a product of HOSOKAWA MICRON CORPORATION), to thereby prepare toner mother particles

having a volume average particle size of 8.5 μm . The quantity of electrification of the thus-obtained toner mother particles was -12 $\mu\text{C/g}$.

[0106]

(External additives)

The external additives externally added to toner mother particles used in Examples are shown in Table 1 below.

[0107]

Table 1

	External Additive	Trade Name	Average Particle Size	Manufacturer
a	Positively electrifiable silica	Positively electrifiable hydrophobic silica	30 nm	Nippon Aerosil Co., Ltd.
b	Titanium oxide	Hydrophobic titanium oxide*)	Long axis: 20 nm	TITAN KOGYO KABUSHIKI KAISHA
c	Long chain fatty acid salt	Magnesium stearate		

*) Rutile-anatase type

[0108]

(External addition process)

In the examples of the present invention, external addition process was performed by adding prescribed amounts of external additives to 100 mass parts of toner mother particles, and stirring the constituents by using a Henschel Mixer FM20B (a product of MITSUI MINING COMPANY, LIMITED) for 3 minutes with Z0S0 type stirring blades at 2,000 rpm. In the manufacturing process of toner B, titanium oxide fine particles and particles comprising a long chain fatty acid or a salt thereof respectively in prescribed amounts to 100 mass parts of the toner mother particles were added to the mixture obtained by externally adding positively electrifiable silica fine particles to toner mother particles, and the mixture was stirred with a Henschel Mixer on the same condition as the external addition condition of positively electrifiable silica fine particles.

[0109]

(EXAMPLE 1: Preparation of toner A)

Toner A was prepared by the external addition process of adding 1.0 mass part of NA50H, 1.0 mass part of STT-30S and 0.2 mass part of magnesium stearate powder to 100 mass parts of the above-obtained toner mother particles. The process is described in Table 2 below.

[0110]

(EXAMPLE 2: Preparation of toner B)

External addition process was performed by adding 1.0 mass part of NA50H to 100 mass parts of the toner mother particles. Toner B was prepared by the external addition process of adding 1.0 mass part of STT-30S and 0.2 mass part of magnesium stearate powder to the above-obtained mixture. The process is described in Table 2 below.

[0111]

(COMPARATIVE EXAMPLE 1)

Toner C of Comparative Example 1 was prepared by the same external addition process as in Example 1 except for adding 1.0 mass part of NA50H and 0.2 mass part of magnesium stearate powder. The process is described in Table 2 below.

[0112]

(COMPARATIVE EXAMPLE 2)

Toner D of Comparative Example 2 was prepared by the same external addition process as in Example 1 except for adding 1.0 mass part of NA50H and 1.0 mass part of STT-30S. The process is described in Table 2 below.

[0113]

(COMPARATIVE EXAMPLE 3)

Toner E of Comparative Example 3 was prepared by the same external addition process as in Example 1 except for adding 1.0 mass part STT-30S and 0.2 mass part of magnesium

stearate powder, and then externally adding 1.0 mass part of NA50H. The process is described in Table 2 below.

[0114]

Table 2

	External Additives			Order of External Addition		
	a	b	c	First Stage	Second Stage	
Example 1	1.0	1.0	0.2	a+b+c	-	Toner A
Example 2	1.0	1.0	0.2	a	b+c	Toner B
Comparative Example 1	1.0	-	0.2	a+c	-	Toner C
Comparative Example 2	1.0	1.0	-	a+b	-	Toner D
Comparative Example 3	1.0	1.0	0.2	b+c	a	Toner E

The numeral in the column of External Additives shows the addition amount (mass parts) to 100 mass parts of toner mother particles.

[0115]

(EXAMPLE 3)

The toners A to E respectively obtained by the above methods (Table 2) were evaluated. Items and methods of evaluations are as follows.

[0116]

1. Liberation rate of external additives (silica fine particles, titanium oxide fine particles):

The liberation rate of external additives (silica fine particles and titanium oxide fine particles) was measured with PT100 Particle Analyzer (a product of

Yokogawa Electric Corporation). The details of measuring method of the liberation rate of external additives are disclosed in patent literature 7 (JP-A-2002-202622). Describing the principle in brief, liberation rate is obtained by introducing toner particles into plasma, exciting the toner particle to emit light, and measuring the intensity and time of the emission. For example, toner particles to which external additive SiO_2 has been added are introduced into plasma, and the emission intensity of SiO_2 in the toner particles is measured. Assuming that the toner particle to which SiO_2 has been externally added is a spherical particle, the particle size of the spherical particle (equivalent particle size) is obtained from the emission intensity. Similarly to the case of the toner particle, the equivalent particle size of the liberated SiO_2 can be obtained from the emission intensity. However, since the emission intensity of the liberated SiO_2 is small, the equivalent particle size is small. Accordingly, the liberated external additive can be distinguished from the toner particles by comparing equivalent particle sizes. Therefore, the liberation rate of SiO_2 can be obtained according to the following equation (X), by obtaining all the detected number of external additive SiO_2 , and taking the number of individuals having smaller equivalent particle size as the number of particles of the liberated external additive.

[0117]

[mathematical formula 1]

Liberation rate = (detected number of liberated
external additive/all detected number of external (X)
additive) x 100 (%)

[0118]

Whether SiO₂ is adhered to a toner particle or
liberated is distinguished by making use of the fact that
SiO₂ adhered to a toner particle emits light synchronously
with the toner particle, but SiO₂ which is not adhered to a
toner particle does not radiate synchronously with the
toner particle and the time of emission deviates from that
of the toner particle (asynchronously). On the basis of
the measured value, the liberation rate can be obtained by
the following equation (Y).

[0119]

[mathematical formula 2]

Liberation rate = (asynchronous count of external
additive/asynchronous count + synchronous count (Y)
of external additive) x 100 (%)

[0120]

A method represented by equation (Y) was adopted in
the present invention. In addition, the measurement of the
liberation rate of titanium oxide fine particles is
performed in the same manner as above by exciting titanium
oxide fine particles to emit light in plasma. The volume

average particle size of toner mother particles can also be obtained, e.g., by making a colorant contained in the toner mother particles emit light in plasma, and obtaining the equivalent particle size.

[0121]

2. Uniformity of quantity of electrification and electrification:

The quantity of electrification of a toner is measured as follows with E-SPART Analyzer (manufactured by HOSOKAWA MICRON CORPORATION). Each of the toners prepared in Examples 1-2 and Comparative Examples 1-2 and carrier were mixed and stirred, to thereby electrify the toner. Nitrogen gas was then blown to the mixture of the toner and the carrier to separate the toner and the carrier. In the next place, the quantity of electrification of every toner (Q/m) was measured, and the distribution of the quantities of electrification of the toners was obtained. The uniformity of electrification is judged as follows. In number distribution of the quantity of electrification of every one toner (Q/m), the difference between the quantity of electrification of the maximum frequency (Q_1/m_1) and the value obtained by dividing the total quantity of electrification of the measured toners by the measured count (the number) (Q_2/m_2), i.e., the smaller the absolute value of $(Q_1/m_1) - (Q_2/m_2)$, the sharper is the distribution of the quantity of electrification (uniform), and the

greater the absolute value of $(Q_1/m_1) - (Q_2/m_2)$, the broader is the distribution of the quantity of electrification (nonuniform).

[0122]

As the carrier, KBN100 ferrite carrier (manufactured by Hitachi Metals, Ltd.) was used.

[0123]

3. Electrical resistivity of toner:

Electrical resistivity was measured with a hybrid type electrical resistivity tester model DRT-1 (manufactured by Sankyo Biotics according to JIS B9915.

[0124]

The results of the above evaluation are shown in Table 3 below.

[0125]

Table 3

		a	b	c	Electrical Resistivity ($\Omega \cdot \text{cm}$)	Liberation Rate of Silica (%)	Liberation Rate of Titanium Oxide (%)
		Q_1/m_1 ($\mu\text{C/g}$)	Q_2/m_2 ($\mu\text{C/g}$)	a-b ($\mu\text{C/g}$)			
Example 1	Toner A	-10.59	-13.25	2.66	3.1×10^{16}	0.39	0.51
Example 2	Toner B	-12.11	-14.53	2.42	4.3×10^{16}	0.35	0.52
Comparative Example 1	Toner C	-14.66	-19.26	6.30	9.9×10^{16}	0.45	-
Comparative Example 2	Toner D	-13.65	-19.68	6.03	5.6×10^{16}	0.46	0.89
Comparative Example 3	Toner E	-9.25	-15.73	6.48	8.3×10^{16}	0.86	0.56

[0126]

The results in Table 3 show that in the toners obtained by externally adding positively electrifiable silica fine particles, titanium oxide fine particles and particles comprising a long chain fatty acid or a salt thereof (magnesium stearate: metal soap) to negatively electrifiable mother particles at the same time (Example 1) or in a specific order (Example 2), the liberation of the positively electrifiable silica fine particles and titanium oxide fine particles is restrained, the reduction of the electrical resistivity is controlled, and the electrification is unified without using negatively electrifiable silica fine particles. To compare with the toners obtained by the methods disclosed in patent literature 1 to 3 (Comparative Examples 1 and 2), the advantage of the present invention is apparent in uniformity of electrification, and the liberation rate of positively electrifiable silica fine particles and titanium oxide fine particles.

[0127]

(EXAMPLE 4)

A copier (model LP-9300 manufactured by Seiko Epson Corporation) was charged with a toner (toner B) obtained in Example 2, or a toner (toner D) obtained in Comparative Example 2, and printing of 3,000 sheets was performed. Printing was begun when 5% of each toner was consumed, and

the quantity of electrification and the liberation rate of positively electrifiable silica fine particles and titanium oxide fine particles before and after printing were compared. The results obtained are shown in Table 4 below.

[0128]

Table 4

		a	b	c		Electrical Resistivity ($\Omega \cdot \text{cm}$)	Liberation Rate of Silica (%)	Liberation Rate of Titanium Oxide (%)
		Q_1/m_1 ($\mu\text{C/g}$)	Q_2/m_2 ($\mu\text{C/g}$)	a-b ($\mu\text{C/g}$)				
Example 2 (Toner B)	Initial stage	-12.11	-14.53	2.42		4.3×10^{16}	0.35	0.52
	After printing 3,000 sheets	-13.34	-15.36	2.02		4.6×10^{16}	0.41	0.65
Comparative Example 2 (Toner D)	Initial stage	-13.65	-19.68	6.03		5.6×10^{16}	0.46	0.89
	After printing 3,000 sheets	-21.39	-30.65	9.26		4.9×10^{18}	0.88	0.91

[0129]

As is apparently seen from the results in Table 4, the toner in Example 2 (toner B) obtained by externally adding positively electrifiable silica fine particles, titanium oxide fine particles and particles comprising a long chain fatty acid or a salt thereof (magnesium stearate: metal soap) to negatively electrifiable mother particles in a specific order can restrain the fluctuation of the quantity of electrification, the change in the electrical resistivity (increase) and the liberation rate of positively electrifiable silica fine particles and titanium oxide fine particles with the increase of the number of sheets of printing, thus the long term stability of toner can be obtained. On the other hand, in the toner in Comparative Example 2 (toner D) wherein magnesium stearate was not used, the quantity of electrification largely changed, the change in the electrical resistivity was conspicuous, and the liberation rate of titanium oxide was great.

[0130]

[Effect of the Invention]

A toner obtained by adding positively electrifiable silica fine particles, titanium oxide fine particles and particles comprising a long chain fatty acid or a salt thereof (magnesium stearate: metal soap) to negatively electrifiable mother particles at the same time, and a

toner obtained by externally adding titanium oxide fine particles and particles comprising a long chain fatty acid or a salt thereof after positively electrifiable silica fine particles have been added are excellent in the restraint of the liberation rate of positively electrifiable silica fine particles and titanium oxide fine particles, the reduction of electrical resistivity is restrained in these toners, and they are excellent in uniformity of electrification. Further, the change in the quantity of electrification, the change in the electrical resistivity (increase) and the liberation of positively electrifiable silica fine particles and titanium oxide fine particles with the increase of the number of sheets of printing can be prevented, thus the long term stability of toner can be obtained. Further, since it becomes possible to obtain good electrification characteristics and flowability without using negatively electrifiable silica fine particles, the set temperature of a fixing chamber in fixing a toner can be made low, and at the same time, good image strength can be ensured.

[Designation of Document] ABSTRACT

[Abstract]

[Problem] To provide a toner which is low in desorption of silica fine particles or titanium oxide fine particles, which can maintain the electrification property for a long period of time, shows high flowability.

[Means for Solving the Problem] The toner of the present invention is obtained by externally adding positively electrifiable silica fine particles, titanium oxide fine particles and particles comprising a long chain fatty acid or a salt thereof to negatively electrifiable toner mother particles. Preferably, the toner of the present invention is obtained by adding these additives at the same time to toner mother particles having the quantity of electrification of from -5 to $-60 \mu\text{C/g}$, or adding titanium oxide fine particles and particles comprising a long chain fatty acid or a salt thereof after adding positively electrifiable silica fine particles. Since it is possible to obtain good electrification characteristics and flowability without using negatively electrifiable silica fine particles, the set temperature of the fixing chamber of a toner can be made low, and at the same time, good image strength after fixing can be ensured.

[Representative Drawing] none